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13. ABSTRACT (Maximum 200 words)  Nanomaterials synthesis and characterization have been very active development fields for many years, motivated by the prospect of extremely high mechanical properties coupled with useful plasticity and elevated temperature properties. We will briefly review the history of nano-materials research, describe the principal synthesis routes for particles, and review the availability of consolidation technology capable of producing shapes which may demonstrate the physical properties which researchers have predicted and expected. We have concluded from our review and from our own research in nanomaterials, that much more effort now be invested in consolidation development in order to begin the commercialization of nanograined solids as engineering materials. We will emphasize consolidation process efforts which, for the most part, seem to be in their infancy with regard to nanomaterials.				
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## ***Introduction***

Nanoparticle materials have been an active materials development topic for ten to fifteen years - longer if one accepts amorphous metals and rapid solidification rate (RSR) structures as related activities. It is our intent in this paper to offer a brief overview of such development efforts and a review of potential nanomaterial consolidation methods. Further development of such consolidation techniques is, in our opinion, a significant opportunity which could accelerate the engineering application of nanomaterials. Of course such consolidation methods must preserve the nanometer grain sizes of the starting materials in order to preserve their expected advantages in physical properties through scale up to engineering application. As we will see, there has been limited effort to consolidate nanoparticles to specimen volumes useful for physical property measurements. We have been able to identify two efforts to demonstrate commercial prototype applicability for nanoparticulate components. Recent developments of so called "fast consolidation" processes provide an opportunity to consolidate nanoparticulate materials so as to verify their (expected) elevated properties.

We will illustrate the breadth of activity in nanoparticle fabrication, including our own process, without going into the depth of chemical process detail and characterization beneath. Activities in fast consolidation of fine particles are more difficult to document because of commercial requirements to "produce product" rather than a detailed technical understanding (and documented literature) of the process. Some consolidation processes while represented in the technical literature have not been applied to nanoparticle consolidation. We have found that (again, with the two exceptions noted above) processes which emphasize commercialization have primarily consolidated more typical powder metallurgy materials in the 1 to 50 mm particle size range.

The lack of consolidation activities on nanoparticulates is explained primarily by a lack of sufficient quantities of nanoparticulate materials to permit proper process development and physical property studies. We have identified at least 10 processes which are capable of such consolidation. In at least 3 instances initial experiments have begun on nanoparticulate consolidation.

## ***Nanoparticulate Synthesis Processes***

The history of research and development on materials having ultrafine structures can be traced to the middle to late 1800's. Sorby and Sauveur in the early 1900's, pioneered the study of the microstructure of steel and its effect on physical properties, including the influence of martensite (and its very fine microstructure) on mechanical properties. These activities established the field of ferrous metallurgy and the study of processing-microstructure-physical property relationships. Nonferrous metallurgy investigation followed very quickly along with analogous efforts in nonmetallic (ceramic) systems.

In the following paragraphs, we detail some of this history emphasizing developments in the 1970's and 1980's when "Rapid Solidification Rate" (RSR) processes and structure were very actively explored as well as activities up to the present time directly involved with nanomaterials synthesis, consolidation, and properties.

In a review on the development of materials having "ultrafine microstructures," Gleiter (1) points

out that the control of the microstructure on a submicroscopic scale has been recognized for many years to be technologically important. He mentions the work of early metals physicists (before the field of "metallurgy" was established) such as Sauveur, Sorby, Tschernoff, et al for pioneering work on the nature of ultrafine microstructures and their effects on macroscopic, engineering properties. Some of this work began in the late 1800's and early 1900's. Gleiter (1) cites Wilm's discovery of precipitation hardening in an Al-Cu-Mg-Mn alloy in 1906 as an example of the early recognition of the effects of "fine scale" microstructure on macroscopic properties of nonferrous metals. Sorby and others as mentioned above had already pointed out the importance of such structures on the properties of ferrous alloys. It remained for Merica and others in 1919 to propose that the hardening observed by Wilm was due to the precipitation of a new phase on a submicroscopic level.

These early examples of the recognition of the influence of submicroscopic structure on mechanical properties of metals were followed in the 1970's by the successful manipulation of electronic properties (especially magnetic effects) of metals and non metals. Ceramists in the 1980's generated new materials on a nanoscale by the use of sol gel synthesis, a continuing area of activity today. Nanometer scale electronic devices incorporating quantum wells were created using the sol gel method and demonstrated important technological features (2).

One of the earliest groups to intentionally fabricate materials with amorphous, metastable structures was P. Duwez, et al (3) at the California Institute of Technology. Their development of "splat cooling" was rapidly followed by other approaches to ultra fast quenching from a melt thereby creating a group of techniques termed rapid solidification rate processing or "RSR" technology. Even though there were many uses for the amorphous "glassy" metals developed initially, it was also observed that devitrification did not necessarily destroy the interesting properties of the amorphous material but in some instances resulted in enhanced properties. Recrystallized amorphous materials, while generally creating microstructures in the submicron range (100 to 1000 nanometers), have also been observed to recrystallize in the 10 to 100 nanometer range. Examples of glassy metal systems exhibiting devitrification to nanocrystalline structures are Zr-Hf-Ni (4), Gd-Fe (5), and Zr-Ni (6).

Amorphous materials have found limited commercial use as low-loss transformer core materials and as specialty braze alloy materials following the work of Duwez et al (3). Their experiments in very fast cooling rates ( $\sim 10^6$  °C/sec) which they achieved by "splat cooling," produced "glassy" or amorphous metals. An interesting review of the development and commercialization of these materials was presented by J.J. Gilman (7). He describes in detail the evolution of glassy metals from laboratory scale through the development of production scale fabrication technologies to commercial viability through an Allied Signal/Mitsui joint venture. During this process, the Electric Power Research Institute (EPRI) supported the development of materials specific to the power distribution transformer market. The generic product name associated with the Allied Signal/Mitsui material was METGLAS™. Magnetic shielding consisting of woven ribbons of METGLAS was called METSHIELD™ and resulted in the first commercially successful use of METGLAS (7). Brazing foils were the second followed by other applications. For example, antipilferage devices were developed which exploit the nonlinear magnetic response of metallic glasses to radio waves. One interesting ancillary effect of amorphous metals was observed in the mid to late 70's at Allied - the fact that devitrified glassy metals have very useful, in some cases superior, physical properties in themselves. Gilman (7) describes the synergistic development of DEVITRIUM™ alloys and their use in replacing cobalt alloy tool steels and even some of the cobalt

bonded WC tools having lower WC contents (i.e. the "high impact" grades).

Savage and Froes (8) present a detailed description and comparison of RSR processes; their development, advantages and disadvantages. In this discussion of RSR technology, they describe the evolution of twenty six distinct processing routes resulting in powders, ribbon, "splat" particles, flakes, or surface layers having amorphous or ultra fine crystalline structure. In most cases larger particles (10 to 100  $\mu\text{m}$ ) were produced which possess an internal structure which is amorphous or microcrystalline. Some amorphous alloys were devitrified to grain sizes of 100 Å, or 10 nm and were very homogeneous (9).

Savage and Froes divide RSR techniques into two groups: those which generate liquid droplets ("atomization") and those which generate an extended melt stream or surface which is then solidified rapidly (e.g. into ribbons or foils). Table 1 in their paper gives a comprehensive list of RSR techniques, describes the morphology of materials produced and techniques that are particularly suited to the different materials.

An interesting, but little explored, processing route to amorphous and crystalline powders is precipitation from electroless and electrolytic plating solutions. Reports of research in this area have been published by Meisel (10), Wurtz (11), and Brenner, et al (12,13). Particle sizes down to 500 nm were demonstrated, but this is currently not an active area of development.

Sputtering is another technology that is being explored in many countries. We have found references to efforts in Hong Kong (14), Australia (15), the United States (16-20), Japan (21) and the People's Republic of China (22). No significant quantities of particles seem to have been produced and we can find no references to consolidation work on sputtered nanoparticles.

Milling has been a popular and productive approach to the fabrication of many microcrystalline, nanocrystalline and amorphous materials. An exhaustive review of these activities would be very lengthy, but we should present some examples of this technology. In Europe, Matteazi (23-25) worked with III/V materials (24), Al reduction of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) (25), and (with LeCaer-23) preparation of silicides, stannides, germanides and aluminides. Politis (26,27) has explored preparation of germanides (26,27) and metallic alloying reactions such as Ti/Cu.

In the United States many researchers have used the milling approach. Representative activities have been reported at the California Institute of Technology (28,29), North Carolina State University (30,31) and the University of Maryland, Baltimore County (32,33). ALCOA (34,35) personnel have attempted to understand the evolution of the mechanical alloying process. Systems explored include Cr-Fe (28), Zr-Al (29), various brittle materials such as Si-Ge (30),  $\beta$ -brass from copper and zinc (31), reduction of oxides, e.g.  $\text{Fe}_2\text{O}_3$ , by Al (32), and  $\text{Al}_2\text{O}_3$  as an additive to the Al/ $\text{Fe}_2\text{O}_3$  system to control thermal energy (33).

Spark erosion is an evolution of electrical discharge machining (EDM) in which material is removed from a work piece by the thermal shock and local melting caused by small arcs (sparks) formed by passing a high frequency current through a graphite electrode (having the finished shape) to the workpiece (bathed in a dielectric fluid). Exploratory work has been done in Japan (36), the FSU (37)

and the United States (38,39). The authors have demonstrated the feasibility of producing nanoparticles of tungsten (40) and intermetallic materials (41) using this technology. We will describe these efforts in more detail below.

It would be particularly attractive to produce nanoparticles of ceramic materials and ceramic matrix composites. Materials engineers have generally not been able to commercialize monolithic structural ceramics (e.g., components for heat engines applications) because state of the art materials simply do not have adequate strain to failure and flaw tolerance. An interesting early demonstration of nanophase ceramics in the form of particles and coatings was done at the Air Force Materials Laboratory by Mazdidasni and Lynch (42) by starting with alkoxides. They demonstrated coatings of  $ZrO_2$ ,  $HfO_2$ , and others as well as building and demonstrating apparatus to vaporize the alkoxides to form particulates.

Recent work in ceramic materials has combined both normal particulates (including "submicron") and nanoparticles with fast consolidation techniques such as microwave assisted sintering (43,44) and plasma assisted sintering (45). It is interesting to note that ceramic nanoparticulates seem to be easier to consolidate (46) possibly because of superplasticity effects (47).

We have identified three routes to produce nanoparticulate ceramics: sol-gel synthesis followed by drying and crushing or spray drying, gas phase condensation from a vapor, and gas phase reactions driven by laser irradiation or furnace deposition (i.e. analogous to chemical vapor deposition). Examples of systems described in the literature are diamond particles (as "drug delivery" media) (48), pure oxides (e.g.  $Al_2O_3$ ,  $ZrO_2$ ,  $TiO_2$ ,  $MgO$ ,  $SiO_2$ ), mixed oxides (e.g. mullite,  $Y_2O_3/ZrO_2$ ,  $Al_2O_3/TiO_2$ ), carbides (SiC), nitrides ( $Si_3N_4$ ), mixed oxycarbides ( $Al_2O_3/SiC$ ,  $MgO/SiC$ ), and mixed carbonitrides ( $SiC/Si_3N_4$ ), to oxycarbonitrides (Si-C-O=N).

Nanophase Technologies (Darien, IL) has been developing the gas phase condensation approach (49) in conjunction with researchers at Argonne National Laboratory (Argonne, IL) and the University of Illinois (Urbana, IL) (50-52). They have synthesized and consolidated  $TiO_2$  as well as other ceramics such as alumina, chromia, yttria, titania, zirconia, silica, ceria in quantities ranging from grams to kilograms ( $Al_2O_3$  and titania) having particle sizes between 5-50 nm, mostly in the 10-20 nm range according to company literature. They produce nanosized clusters of the desired compounds above an evaporation source which may be joule heated, sputtered or electron-beam heated. A convection current is then established between the source and a cooled collection plate or cylinder nearby where the clusters condense and are collected. This technology is traceable to H. Gleiter in Germany (49) and has been developed by researchers at Argonne National Laboratory (Argonne, Ill), the University of Illinois (Urbana, Ill) as well as Nanophase Technologies (Darien, Ill) (50-52). The references cited emphasize the fabrication, consolidation and mechanical testing of  $TiO_2$  nanoparticles. Both pressureless and pressure assisted sintering (to ~ 99% theoretical) take place at temperatures (400-600° C) below those required for densification of powders 500-1000 X larger. Furthermore, surprisingly large deformation was achieved in uniaxial compression testing at 800-900° C (approx  $0.5T_m$ ) - 0.6 true strain. This indicates a tendency to superplastic flow at temperatures drastically below those at which other ceramics have exhibited superplasticity. Such behavior was demonstrated for nanocrystalline  $TiB_2$  in Ref 44. Nanophase also produces nanometer particles of various metals (e.g. Cu, Ag, Al, Ni and Au) and can furnish some of them dispersed in  $\alpha$ -Terpenol.

There are many theoretical reasons to suggest that moving to a finer particle size will improve both processing and property characteristics of structural ceramic parts. In particular, grain sizes below one micron permit plastic deformation of some material systems at rates, temperatures and pressures that make forging of ceramic parts a possibility on an industrial basis. At this time, consolidation of single phase nanophase powders to full density while maintaining nanometer grain size is a difficult problem due to the inherent metastability of the powders and a strong tendency for rapid grain growth. A Nanophase Technologies Corporation ATP project is approaching this problem by characterizing the processing and properties of multiphase oxide systems. Mutually insoluble grains can stabilize each other against grain growth, providing full density while maintaining a nanometer grain size. The ultimate goal of this project is the fabrication of engine and manufacturing process ceramic parts through forging, largely eliminating the costs and technical drawbacks of machining (53).

ZrO<sub>2</sub> (54) and Y<sub>2</sub>O<sub>3</sub> (55) stabilized ZrO<sub>2</sub> particles have been prepared by sol gel techniques and then sintered or hot pressed by conventional techniques. Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub> particles (55) 40 nm in size coarsened to 70 nm on annealing at 1273°K. The powder was then hot pressed in an alumina die without cold forming. The powder (under 23 MPa pressure) was then heated to between 1290 and 1570°K hold temperatures for 60 minutes. The authors studied densification kinetics and determined that full density could be reached at temperatures of 1500°K to 1600°K with "minimal grain growth" although the authors present no microstructures of fully dense material.

Laser irradiation of gaseous mixtures has also been demonstrated to produce nanoparticles by French researchers for SiC (56) and by Japanese researchers for SiC/Si<sub>3</sub>N<sub>4</sub> (57). They also refer to other laser synthesis activities in the literature to produce particles of B<sub>4</sub>C, B, TiB<sub>2</sub>, S-C-N, Fe-Si-C, FeSi<sub>2</sub>, TiO<sub>2</sub>, and ZrB<sub>2</sub>. In the case of pure SiC, 30 grams per hour up to 100 grams per hour were produced with particle sizes ranging from 10-50 nm (equiaxed) and having a narrow size distribution depending on laser intensity, gas pressure and flow rate. Many details of the chemistry and the characterization of the powders are presented but no consolidation experiments were reported.

The chemistry of SiC/Si<sub>3</sub>N<sub>4</sub> nanocomposite particles (57) could be controlled over a wide range of carbon and nitrogen contents (0-30 wt%). Particle sizes ranged from 5-10 nm up to 100-200 nm depending on consistent gas flow rates. Amorphous phases (Si,  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>,  $\beta$ -Si<sub>3</sub>N<sub>4</sub>) were also observed under some conditions. Specific surface area, SEM-TEM, XPS, EELS and XRD characterization of the various powders produced are related to preparation parameters. As in Ref. 55 no consolidation work was reported.

An example of chemical vapor deposition synthesis of nanoparticles was presented by French researchers (58). They deposited 200-300  $\mu$ m thick coatings of SiC/TiC onto Mo substrates. Either nanocomposites or microcomposites were obtained depending on deposition conditions. Needlelike TiC was produced in all cases but in one deposition parameter regime they were 8 to 10 nm thick with lengths up to 300 nm. Needles were always oriented with long axes parallel to the growth direction (perpendicular to the substrate).

In more recent studies (40,41) researchers at MMI have used the pulsed reactive electrode (PRE) method to synthesize nanoparticles of W, W-2%Th, Ta, NiAl and FeAl. They have used electrodes immersed in dielectric fluids to create nanoparticles that range from 10-100 nm. These researchers also

found that they could produce whiskers, platelets and spherical powders depending on the choice of the process conditions. They attributed this flexibility to the inherent process conditions of the electrodes and are continuing to research in this area. They aim to produce quantities exceeding 5-8 Kg/day from a single machine that is designed specifically for the creation of nanoparticles. This machine will also be capable of producing most metals, conductive ceramics and composites.

In testimony to the interest of materials engineers in nano-sized materials, some companies have begun to provide such materials on a commercial basis. We list them below with brief descriptions of materials available and the technology used to fabricate them. We make no efforts to describe the characteristics of these materials or to comment on the companies themselves, lest one or another such description appear critical and to prevent one or another such description from appearing to endorse or favor one company over another. We have included two companies which provide "micron" and "sub-micron" materials as well.

Fujimi America (Wilsonville, OR) - parent company, Fujimi, Inc., (Nagoya, Japan) provides "precision classified" powders down to the submicron particle size range (59).  $\text{Al}_2\text{O}_3$  is produced in Oregon and SiC is also available. Their powders are being used as component materials in metal matrix and ceramic matrix composites, microelectronic packaging, computer heads and as wear resistant fillers for paints coatings and papers.

Micron Powder Systems/Hosokawa Micron International Inc., (Summit, NJ) manufactures a piece of equipment which incorporates a stationary "shoe" and a scraper enclosed within a rotating drum chamber. Particles of material to be reduced and or mixed are held against the chamber wall and subjected to compression, shearing, attrition and rolling forces which are determined by the clearance between the shoe and the chamber well.

Nanodyne is the world's only manufacturer of Nanograin™ composite powders whose WC grain sizes are 20 to 40 nm, which are 10 to 20 times smaller than those available in the finest conventional micrograin powders. In Nanodyne's spray conversion process, Nanocarb™ powder is made by first drying an aqueous solution of salts of tungsten and cobalt to make a precursor powder. This powder is then converted by a series of thermodynamically controlled gas/solid reactions to produce powder whose WC grain size is independent of particle size. A typical powder particle consists of a hollow, porous 75 micron sphere containing hundreds of millions of WC grains in a cobalt matrix. Because the process begins with a solution, the constituents of Nanocarb powder are mixed on the molecular level. There is no milling involved and the process is sealed to the environment from the start. Other binders which may be used besides cobalt include nickel and iron. Products made from Nanocarb powder have an extremely fine grain size and uniform microstructure and are much harder at a given toughness and tougher at a given hardness than products made from conventional micrograin powders. Hardness of parts made from Nanocarb 11% Co powder equals that of the finest conventional 7% Co powders. Nanodyne's current production capability exceeds 100 tons per year. Companies are now evaluating the powders for printed circuit board drills, industrial rotary cutting tools, indexable cutting inserts, wear parts, mining tools, and thermal spray coatings (60).

A former Soviet Union (FSU) company, Server (Talinn, Latvia) has advertised metal powders available in grams to kilogram quantities produced by an exploding wire technique. Elemental metals,

alloys and some compounds are available - the latter by producing the reaction in the presence of nitrogen. Particle sizes are in the 0.1-0.5 micron range (100-500 nm). Materials mentioned specifically are aluminum nickel-chromium alloy, copper, tungsten, tantalum, iron nickel, molybdenum, niobium, titanium, a copper-tin alloy and a copper-zinc alloy. They claim a plant production rate of 200 grams/hour of aluminum and up to 1000 grams per hour of tungsten.

A brief review of ceramic nanostructured materials was published in 1986 (63). The authors describe what may be generally termed preceramic polymer process routes. They mention hydrolysis of sol gels, thermal decomposition of organo-metallic polymer, wet chemical processing, hydrothermal, flame/plasma spray, and spray decomposition, presenting 49 references which give details on the major approaches. A cursory research of the literature reveals the following ceramic nanostructured compounds in addition to those mentioned above (Pb, Ba) TiO<sub>3</sub>, CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, mica based glass ceramics, Al<sub>2</sub>O<sub>3</sub> - SiC and mullite.

We may summarize the availability of nanoparticle materials in the US by stating that there are two companies - Nanophase Technologies and Nanodyne which are offering materials for sale and are developing consolidation processes.

### ***Fast Consolidation of Fine Particles***

In attempting to predict nano material mechanical properties, it is tempting to invoke the Hall-Petch (62,63) relationship between yield stress and grain size of a material:

$$\sigma = \sigma_0 + fd^{-1/2}$$

where  $\sigma$  is the yield stress,  $\sigma_0$  is the lattice frictional stress which must be overcome for dislocation movement,  $f$  is a constant, and  $d$  is the grain size. If yield stress (or a property related to yield stress such as hardness) is plotted vs  $d^{-1/2}$ , a straight line with positive slope,  $f$ , results if the Hall-Petch relationship is valid. There may be a limit to the use of this relationship, however, when grain sizes become small ( $<1 \mu\text{m}$ ) implying that the volume fraction of grain boundary or interface structure becomes appreciable - and begins to significantly influence mechanical properties. Chokshi, et al (64) show that microhardness measurements on OFHC coarse grained copper ( $d$  between 4 and 25  $\mu\text{m}$ ) at ambient temperature are consistent with the Hall-Petch relationship. In contrast, nanocrystalline copper ( $d$  between 6-16 nm) hardness data, while falling on a straight line plot vs  $d^{-1/2}$ , exhibit a negative slope with decreasing grain size. Microhardness data for nanocrystalline palladium behave similarly to copper. The authors rationalize these data on the basis of diffusional creep occurring across or along grain boundary regions aided by the stress exerted by the indentation process. They show, by order of magnitude calculation using the Coble creep expression that the deformation rate of nanocrystalline copper by this mechanism should be comparable to or greater than plastic deformation due to intragranular dislocation motion. The latter mechanism is the primary response to hardness measurements in materials where  $d \geq 1 \mu\text{m}$ . Indeed we may speculate that this is one of the contributing mechanisms to rapid deformation at much lower temperatures than "normal" which can aid in near net shape forming of nanocrystalline materials including ceramics (46,52).

Two consolidation techniques currently being developed are (pressureless) microwave assisted sintering, and plasma activated sintering (PAS). Major proponents of these technologies are Northwestern University - microwave sintering and the University of California (Davis, CA) - plasma activated sintering. Both of these technologies incorporate "fast" processes, i.e. minutes, not hours, to achieve essentially theoretical densities. This very short time is important for two reasons. First, economic viability must incorporate short turn around times and near net shape capabilities. Advanced materials processing and fabrication is evolving in this direction. Second, short times and low(er) temperatures are needed both to conserve energy (again, minimize cost) and minimize grain growth of extremely fine (and very active) particles. Aside from the obvious difference that the U.C. Davis process incorporates uniaxial pressure, both processes take advantage of microwave activation of surfaces of particles, an effect which has an uncomplicated name but whose phenomenology is very poorly described or understood. Detailed descriptions of both processes follow.

Sintering of materials in the presence of a plasma has been researched since 1968 (65). During the past 10-12 years, D.L. Johnson, et al, at Northwestern University (Evanston, IL) performed extensive work on the sintering of oxides in the presence of plasmas (66,67). Their process development has emphasized  $\text{Al}_2\text{O}_3$ . References 68 and 69 present examples of fabrication experiments on MgO doped  $\text{Al}_2\text{O}_3$  having very fine grain size (submicron-0.3  $\mu\text{m}$ , Ref. 68 and high surface area - 30  $\text{m}^2/\text{g}$ , Ref. 69). MgO contents were 0.25 wt% in both cases. Plasmas were either argon (68) or nitrogen (69) and were supported by high frequency generators (5 MHz/argon, 25-40 MHz/nitrogen). The specimens were dried (excessive water vapor could quench the plasma) and isostatically pressed. Densification was accomplished by translating the pressed rods or tubes through the plasma zone, a "zone sintering" process, while rotating the specimen to promote temperature uniformity. Undoped  $\text{Al}_2\text{O}_3$  did not reach full density (96%) nor did it reach the same density as MgO doped  $\text{Al}_2\text{O}_3$  treated similarly (98%) (68).

Other efforts have attempted to optimize some of the sintering parameters and correlate this with the microstructural features such as grain size, porosity, type / distribution / amount of the porosity (69). The authors relate sinter density and final (avg) grain size to plasma gas pressure, sintering temperature and total time (at one gas pressure). Sintered densities ranged from slightly less than 99% to 99.8% of theoretical at a sintering time of 800 to 1000 seconds with a final grain size of 5 to 10  $\mu\text{m}$  in rod specimens.

Japanese researchers (70) have studied the sintering of  $\text{Si}_3\text{N}_4$  "ultrafine, amorphous powder (30 nm)" in a plasma of  $\text{N}_2/\text{H}_2$ . They observed no densification beyond the 50 to 55% achieved by cold pressing. Grains grew to 0.3  $\mu\text{m}$  near the surface of a 5 mm diam. x 1 mm thick compact when heated for 1 min at approximately 1900°C. Temperatures were obtained from extrapolation of cooling curves. Weight loss and changes in the ratio of  $\alpha\text{-Si}_3\text{N}_4$  to  $\beta\text{-Si}_3\text{N}_4$  were observed. The 30 nm particles were produced by a plasma synthesis process. No SEM or TEM characterization of starting powder particles was presented.

A research team at the University of California (Davis, CA) has been exploiting a plasma sintering process (equipment built by Sodick Inc., Yokohama, Japan) in which the compaction is accelerated by the application of up to 50 MPa uniaxial pressure to the consolidating body (45). In contrast to the Northwestern group the U.C. (Davis) team has explored metals, intermetallics, oxides, and covalently bonded materials such as SiC and AlN (45). They have consolidated materials with

average particle sizes from 0.1 to 44  $\mu\text{m}$  including mechanically alloyed materials - all apparently retaining close to the starting particle size in the consolidated specimen. They have also consolidated nanophase (mechanically alloyed)  $\text{Nb}_3\text{Al}$  (71).

It is encouraging that the PAS process is used commercially in Japan by Matsushita, Inc. for producing hard magnet materials (72). In the PAS process, densification is achieved by a combination of resistance heating with pressure application and plasma generation among the powder particles. The loose powders are loaded in a graphite mold and die unit followed by a modest uniaxial pressure and a pulsed electrical discharge application. Typically, the uniaxial pressure is in the order of 10-15 MPa and the electrical discharge of 750 A and 25 V is applied for 30 seconds in equal on and off pulses of 80 ms. In the next step, a high DC current (600-2000 A) promotes joule heating of the powder particles while the same or different pressure level is applied. The time for high temperature and pressure application is short, usually in the order of minutes to reach full densification. Materials that have been PAS consolidated include difficult-to-sinter materials such as covalent ceramics, oxygen sensitive intermetallic compounds and superconductors. For instance, PAS consolidation to near theoretical density of deliberately additive-free AlN powders was recently reported to take place in 5 minutes (45). This very short time exposure at high temperature permitted full densification with minimum microstructural changes. In particular, the initial submicron grain size of Al powders was retained in the final microstructure.

There are other examples of developing fast consolidation technology. Explosive forming has been successful in bonding of layers or discrete plates of metallic materials. However, many attempts to consolidate particles of metals, ceramics and metal/ceramic composites have not been successful in that an in-homogeneous and usually cracked body results. There are some variations on the theme of "fast HIPing" (fast, hot isostatic pressing) which are achieving success - mostly with powdered metals, but sometimes with ceramics and ceramic/metal composites. The latter two types of materials are decidedly more difficult to consolidate to full density. It is important to remember that except for one type of process (two companies) to be described, the other fast HIPing processes are only quasi-isostatic, i.e. there is a crystalline solid or molten/solid pressure transmitting medium. The consolidation activities we will describe briefly are:

- ◆ Ceracon, Inc.
- ◆ Superior Graphite Co.
- ◆ Boride Products (Dow Chemical Co.)
- ◆ Forged Performance Products, Inc., and
- ◆ Conaway Technologies, Inc.

All are commercial operations and all have emphasized metals, at least initially, and have attempted MMC and some ceramics.

Ceracon (Sacramento, CA) has developed and is commercializing a fast quasi-isostatic HIP process which uses a granular ceramic material as the pressure transmitting medium rather than the gases used in classical HIP autoclaves. A preform of the material to be consolidated is preheated and transferred to the die containing the hot ceramic medium. Pressure is then applied uniaxially (single acting ram) to the ceramic medium which transmits the pressure quasi-isostatically to the preform.

Canning may or may not be necessary depending on temperature of consolidation and potential preform/medium interactions. Pressures as high as 180,000 psi (1.24 GPa) can densify metals and possibly intermetallics in 1 or 2 minutes. Ceracon has worked with many metals, intermetallics and some metal matrix/ceramic particle composites including cemented carbides.

Superior Graphite (Chicago, IL) in cooperation with the Basic Industry Research Lab (BIRL) of Northwestern University (Evanston, IL) has developed a process called Electroconsolidation. The pressure transmitting medium (graphite) permits the part preform to be heated much more uniformly (by Joule heating of the graphite) and eliminates the tedious separate heating of the preform in the Ceracon process. However, one must coat the preform (e.g. with BN) to protect it from reaction with the graphite. Temperatures to 3000°C are possible and a 100 metric ton uniaxial press is available. Inert gas atmospheres can be circulated through the pressure transmitting medium. Again, cycle times of minutes are achievable. A special grade of graphite grain was developed for this process which withstands repeated cycles and transmits pressure very effectively without sintering - a problem which limits the operating temperature and total time for the Ceracon media before recycling is necessary. Superior has consolidated SiC and Nd-Fe-B magnet materials. Reference 73 describes recent advances in the electroconsolidation process.

The Dow Chemical Co. has been commercializing an inorganic "fluid die" fast forging process termed rapid omnidirectional compaction (ROC). A preform (up to 60-70% dense) is preheated and then embedded in or surrounded by a ceramic material which when heated to the consolidation temperature will become molten. At this point uniaxial pressure can be increased to more than 200,000 psi. The molten material surrounding the preform acts as a quasi-isostatic pressure transmitting medium which permits lower processing temperatures - but not so low that potential interaction with the fluid die medium can be ignored. Processing times are of the order of minutes similarly to the Ceracon and Superior Graphite technologies.

There are at least two fast HIPing processes that preserve the truly isostatic nature of conventional HIP in that they utilize hot gases. These processes, also termed hot isostatic forging, are practiced by Forged Performance Products, Inc. (Oak Ridge, TN) and by Conaway Technologies, Inc. (Dublin, OH). Both processes involve proprietary equipment designs which permit very rapid increases in pressure within the chamber containing the preform. Of course, canning or presintering to closed porosity are still required for both processes. Conaway Technology claims to have developed a process called "Quick Can" which has drastically reduced canning time and cost in order to address this problem.

Forged Performance Products (FPP) equipment can reach pressures of 60,000 psi on components preheated to 1100 to 1150°C in a separate furnace. They have emphasized consolidation of metals such as Ti alloys and tool steels which have been hot isostatically forged (HIF) to 99.5% of theoretical densities of 68 to 78% (cold isostatically pressed). FPP has also experimented with SiC<sub>p</sub>/Ti composites as well as Y<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> ceramics. As with other "fast" consolidation processes, time under pressure is 2 to 10 minutes. Process temperature reductions of 100 to 400°C have been observed for HIF with respect to conventional HIP temperatures for the same materials.

Conaway Technologies' version of hot gas forging is called "Quick HIP." They claim pressure capabilities to either 100,000 psi or 20,000 psi in two chambers both of which have internal furnaces

capable of at least 1300°C. Pressure transmission media are hot gases or particulates such as  $\text{Al}_2\text{O}_3$  and graphite. Metals, intermetallics, and intermetallic composites (Ni aluminide +  $\text{ZrO}_2$ ) have been consolidated to full density at temperatures up to 1050°C and pressures of 60,000 psi for 1 minute. Their 20,000 psi chamber can contain components approximately 5 inches in diameter by 8 to 10 inches long, while the 100,000 psi chamber is limited to components 2 inches diameter by 4 inches long. Process economics and process theory are discussed by R. Conaway (74,75). Lin and German (76) present a comparison of Quick HIP with other sinter and HIP processes to fabricate carbonyl iron powder, preformed by PIM. They found comparable or elevated properties for specimens presintered at 1200°C followed by Quick HIP at 805°C and 500 MPa. Total Quick HIP time was less than 1 hour, while conventional HIP time was 3 hours including 1 hour at maximum temperature and pressure with the same preform treatment as for Quick HIP.

### ***Summary***

The rapid increase in the number of research efforts devoted to the study of nanomaterials has resulted in the development of a number of both conventional and unconventional approaches to their synthesis and consolidation. Without referring to RSR or amorphous materials technology, we may summarize the routes for synthesis as follows:

- ◆ milling/mechanical alloying,
- ◆ sputtering,
- ◆ laser ablation,
- ◆ spark erosion / pulsed reactive electrode,
- ◆ sol gel,
- ◆ vapor condensation, and,
- ◆ spray atomization.

Unfortunately, very few of these routes are capable of even modest scale up to produce kilograms of material which may be consolidated so that physical properties may be measured. At this time, the milling approach has progressed to the point where hundreds of grams (perhaps a kg) may be produced. Questions of contamination, composition control, cost effectiveness and/or further scale up capability remain.

Two commercialization efforts are under way as described above, which include both nanoparticle production and consolidation. We will have to await additional open literature information so as to judge their closely held, essentially proprietary efforts. As described in the references given, these efforts represent vapor phase condensation and a "wet chemical - spray atomization" approach. It is encouraging that one of these companies offers nanomaterials for sale.

University and commercial facilities are pursuing consolidation technologies for fine particles including nanoparticle materials. Such facilities and their technologies (available in the open literature) are:

- ◆ Northwestern University - microwave sintering.
- ◆ University of Kentucky - electrodischarge compaction.
- ◆ University of California/Davis - Plasma and pressure assisted sintering.
- ◆ Superior Graphite - electroconsolidation.
- ◆ Dow Chemical Company - Rapid Omnidirectional Compaction (ROC).
- ◆ Ceracon - quasi-isostatic compaction.
- ◆ Forged Performance Products - hot gas forging.
- ◆ Conaway Technologies - hot gas forging.

Each technology has promise - and limitations - in the consolidation of nanoscale particulates. The quasi-isostatic and hot gas forging technologies seem to be very effective for small (e.g. mechanical properties) specimens. However, those processes depending on media other than gases have been shown to have scalability problems. The two hot gas forging techniques remain to be adequately demonstrated on nanoparticles. The same can be said of the U. of California/Davis process which though using a commercial piece of equipment (a plus), also must be demonstrated on more nanoparticle compositions and on mechanical test specimen sizes. The ability to scale up this technique to deal with production sized parts is also a near-term requirement.

The challenge of commercialization of structural nanoparticle materials clearly lies in scaling up particle production technologies so that available consolidation technologies can be further challenged and tested. The authors of this paper intend to add one more particle production technology termed as "pulsed reactive electrode (PRE)" into the commercial domain in the next one to two years. We hope to challenge the two facilities which seem to have the clear lead in commercialization efforts currently: Nanophase Technologies and Nanodyne as the PRE technology will have the ability to form a wide range of metals, ceramics and composites.

## *References*

- 1 H. Gleiter, Nanostructured Materials, Vol. 1, No. 1, pp 1-19, 1992.
- 2 Physics and Applications of Quantum Wells and Superlattices, E. Mendez and K. Kiltzing, Plenum Press, NY, 1988.
- 3 W. Klement, R. Willens, and P. Duwez, Nature, Vol. 187, p. 869, 1960.
- 4 R. Schulz, V. Matijasevic, and W. Johnson, Physical Review B, Vol. 30, No. 12, 15 Dec 1984.
- 5 S. Lee and A. Miller, J. of Appl. Phys., Vol. 55, No. 10, pp 3465-3470, 15 May 1984.
- 6 M. Henaff, C. Colinet, A. Pasturel, K. Buschow, J. Appl. Phys., Vol. 56, No. 2, pp 307-310, 15 July 1984.
- 7 J. Gilman, J. of Metals, pp 21-24, April 1984.
- 8 S. Savage and F. Froes, J. of Metals, pp 25-33, April 1984.
- 9 S. Whang, J. of Metals, p. 34, April 1984.
- 10 L. Meisel, P. Cote, D. Quinn, Proc. 3rd Conf. on Rapid Solidification Processing, NBS, Dec 1982.
- 11 A. Wurtz, Compt. Rend., Vol. 18, p. 702, 1844, and Vol. 21, p. 149, 1845.
- 12 A. Brenner, G. Riddell, J. Res., NBS, Vol. 37, p. 1, 1946.
- 13 A. Brenner, D. Couch, E. Williams, J. Res., NBS, Vol. 44, p. 109, 1950.
- 14 S. Ling and H. Wong, J. Vac. Sci. and Tech., Vol. A10 No. 3, pp. 573-575, May/June 1992.
- 15 G. Turner, I. Flaconer, B. Jones, D. McKenzie, J. Vac. Sci. and Tech., Vol. A10, No. 3, pp. 455-

456, May/June 1992.

- 16 R. Shull, U. Atzmony, A. Shapiro, L. Swartzendruber, L. Bennet, W. Green, and K. Moorjani, *J. App. Phys.*, Vol. 63, No. 8, pp. 4261-4263, 15 April 1988.
- 17 G. Chow, *MRS*, Vol. 206, pp. 315-320, 1991.
- 18 G. Chow, R. Holtz, A. Pattnaik, S. Edelstein, T. Schelsinger, R. Cammarata, *App. Phys. Lett.*, Vol. 56, No. 19, pp. 1853-1855, 7 May 1990.
- 19 H. Hahn and R. Averback, *J. Appl. Phys.*, Vol. 67, No. 2, pp. 1113-1115, 15 Jan. 1990.
- 20 F. Kaatz, G. Chow, and A. Edelstein, *J. Mat. Res.*, Vol. 8, No. 5, pp. 995-1000, May 1993.
- 21 T. Motohiro, Y. Takeda, Y. Watanabe, and S. Noda, *MRS*, Vol. 206, pp. 423-428, 1991.
- 22 X. Mei, M. Tao, H. Tan, Y. Han, and W. Tao, *Proc. of Nanophase and Nanocom. Mat. Symp.*, *MRS*, Vol. 286, 1-3 Dec. 1992, Boston, MA, eds. S. Komarneni, J. Parker, G. Thomas.
- 23 P. Matteazzi and G. LaCaer, *Processing of Advanced Materials*, Vol. 1, pp. 135-144, 1991.
- 24 P. Matteazzi and G. Farne, *MRS bulletin*, Vol. 26, pp. 1283-1290, 1991.
- 25 P. Matteazzi and G. LaCaer, "Hyperfine Interactions", Vol. 68, pp. 177-183, 1991.
- 26 C. Politis, *Physica*, Vol. 135B, pp. 286-289, 1985.
- 27 C. Politis and W. Johnson, *Jl. of Appl. Phys.*, June, 1986.
- 28 H. Kuwano, H. Ouyang and B. Fultz, *Nanostructured Materials*, Vol. 1, p 143, 1992.
- 29 H. Fecht, G. Han, Z. Fu, and W. Johnson, *Jl. of Appl. Phys.*, Vol. 67, p. 1744, 1990.
- 30 R. Davis, *Jl. of Metals*, pp. 60-61, Feb. 1987.
- 31 B. McDermott and C. Koch, *Scripta Met.*, Vol. 20, p. 669, 1986.
- 32 M. Pardavi-Horvath and L. Takacs, *Trans. of IEEE*, Vol. 28, p. 3186, 1992.
- 33 L. Takacs, *Materials Letters*, Vol. 13, p. 119, 1992.
- 34 A. Jatkar and J. Benjamin, presented at Int'l Symp. on Mechanical Alloying Kyoto, Japan, 7-10 May, 1991.
- 35 J. Benjamin, op.cit.
- 36 T. Yamaguchi and K. Narita, *IEEE Trans. Mag.*, MAG13, pp. 1621-1623, 1977.
- 37 K.K. Namitokov, *Soviet Physics-Techn. Physics*, Vol. 12, pp. 714-716, 1967.
- 38 A.E. Berkowitz and J.L. Walter, in *Rapid Solidification Processing: Principles and Technologies II*, ed. by R. Mehrabian, B.H. Kear, and M. Cohen, Claitor's Publishing Division, Baton Rouge, LA, pp. 294-305, 1980.
- 39 S.F. Cogan, J.E. Rockwell III, F.H. Cooks, M.L. Shepard, *J. Phys. E: Sci Instru.*, Vol. 11, pp 174-176, 1978.
- 40 J.J. Stiglich, T.S. Sudarshan "Synthesis of Nanomaterials" NSF Phase I SBIR, August 1993.
- 41 T.S. Sudarshan and J.J. Stiglich, U.S. Army Phase I SBIR "Synthesis of Nanocrystalline Tungsten Powder", DAAL01-93-C-4038, July 1993.
- 42 K. Mazdidasni and C. Lynch, TDR 64-269, AD 608043, Sept 1964.
- 43 J. Kim and D. Johnson, *Ceramic Bulletin*, Vol. 62, No. 5, pp 620-622, 1983.
- 44 E. Kemer and D. Johnson, *Ceramic Bulletin*, Vol. 64, No. 8, pp 1132-1136, 1985.
- 45 J. Groza, S. Risbud, K. Yamazaki, *Proceedings of "Plasma Synthesis and Processing of Materials"*, edited by K. Upadhyaya, TMS, 22-25 Feb. 93, pp 85-93, 1993.
- 46 H. Hofler and R. Averback, *MRS*, Vol. 286, pp 9-14, 1993.
- 47 H. Hahn and R. Averback, *Jl. Amer. Cer. Soc.*, Vol. 74, No 11, p 2918, 1991.
- 48 N. Kossowsky, *Materials Technology*, Vol. 8 (1/2) pp 3-4, 1993.
- 49 H. Gleiter, *Progress in Materials Science*, Vol. 33, p 223, 1989.
- 50 R. Siegel and J. Eastman, *MRS*, Vol. 132, p 3, 1989.

- 51 J. Parker, presented at Symp. on P/M in Aerospace and Defense Technology, Tampa FL, 1991.
- 52 H. Hahn, J. Logas, H. Hofler, P. Kurath, and R. Averbach, MRS, Vol. 196, pp 71-76, 1990.
- 53 Alan Thomas, Nanophase Technologies, personal communication, 13 April 1994.
- 54 S. Ramamurthi, Z. Xu, D. Payne, J. Amer. Cer. Soc., Vol. 73, No. 9, pp 2760-2763, 1990.
- 55 D. Bourell, W. Kaysser, J. Amer. Cer. Soc., Vol. 76, No. 3, pp 705-711, 1993.
- 56 M. Cauchetier, O. Croix, M. Luce, Advanced Ceramic Materials, Vol. 3, No. 6, pp 548-552, 1988.
- 57 M. Suzuki, Y. Mariette, Y. Nakata, T. Okutani, J. Amer. Cer. Soc., Vol 76, No 5, pp 1195-1200, 1993.
- 58 M. Touanan, F. Teyssandier, M. Duccarroir, M. Maline, R. Hillel, J. Derop, J. Amer. Cer. Soc., Vol. 76, No. 6, pp 1473-1481, 1993.
- 59 M. Oda, I. Katsu, M. Tsuneizumi, E. Fuchida, S. Katsu, C. Hayashi, MRS, Vol 286, pp 121-30, 1993.
- 60 V. Kevorkian, Nanodyne, personal communication, 11 April 1994.
- 61 B. Bender, R. Ingel, W. McDonough, J. Spann, Adv. Cer. Mat., Vol. 1, No. 2, pp 137-144, 1986.
- 62 E. Hall, Proc. Phys. Soc. London, Vol. B64, p. 747, 1951.
- 63 N. Petch, J. Iron Steel Inst., Vol. 174, p. 25, 1953.
- 64 A. Chokshi, A. Rosen, J. Karch, H. Glieter, Scripta Met. Vol 23, No 10, pp 1679-1684, 1989.
- 65 C. Bennett, N. McKinnon, L. Williams, Nature, Vol 217, pp. 1287-88, 1968.
- 66 D. Johnson, R. Rizzo, Amer. Cer. Soc. Bull., Vol 59, No 4, pp 467-72, 1980.
- 67 D. Johnson, J. Kim, in Sintering Theory & Practice, Mat. Sci. Monographs, Vol 14, ed. by D. Kolar, S. Pejovnik, M. Ristic, Elsevier, Amsterdam, 1982, pp 573-578.
- 68 J. Kim, D. Johnson, Am. Cer. Soc. Bull., Vol 62, No. 5, pp 620-622, 1983.
- 69 E. Kemer, D. Johnson, Amer. Cer. Soc. Bull., Vol 64, No. 8, pp 1132-1136, 1985.
- 70 W. Pan, M. Sato, T. Yoshida, K. Akashi, Adv. Cer. Mat., Vol 3, No. 1, pp 77-79, 1988.
- 71 M. Tracy and J. Groza, Nanostructured Materials, Vol 1, pp 369-378, 1992.
- 72 M. Wada and F. Yamashita, Presented at Intermagnetics Conference, Brighton, U.K., 17-20 April 1990.
- 73 W. Goldberger, B. Merkle, D. Boss, to be presented at 1994 Intl Conf. on Powder Met. & Particulate Mat., 8-11 May 1994, Toronto, Canada.
- 74 R. Conaway, in Metal Working Technology Europe 1993, ed. by Peter Dempsey, publ. by Sterling Publ. Ltd., (ISSN0965-335X), pp 38-41.
- 75 R. Conaway, Advanced Mat. Processes, No. 6, 1989, pp 35-39.
- 76 S. Lin and R. German, Met. Trans. A, Vol 21A, Sept. '90, pp 2531-2538.

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